517,364

CANADA

THE PATENT OFFICE

PATENT No. 517,364 ISSUED OCT. 11, 1955

Stabilized Diazonium Salts and Process of Effecting Same

William H. von Glahn and Herman A. Bergstrom, Albany, New York, U.S.A., assignors to General Aniline & Film Corporation, New York, New York, U.S.A.

Application June 7, 1949, Serial No. 588,733
In the United States October 22, 1948

8 Claims — No drawing

This invention relates to the preparation of stable diazonium compounds and refers particularly to the production of non-dusting diazonium salts or Fast Color Salts of abnormal grain or particle size which can be used effectively as dye intermediates.

In the preparation of diazonium salts, the diazo compound, as produced by diazotization of a primary amine, is generally stabilized by forming a complex double salt of the diazonium chloride with an inorganic salt, such as zinc chloride, tin chloride, cadmium chloride, manganese chloride, sodium fluoroborate, aromatic and aliphatic sulfonic acids, sulfates and chlorides. These are known in the trade as Fast Color Salts (see Saunders, "The Aromatic Diazo Compounds," p. 29, London 1936). In many cases the stabilized diazonium salts thus obtained have fine grain crystals which filter very poorly, due to the particle size, and result in a large proportion of water in the filter cake. The dried product creates dusting problems during grinding and in subsequent processing steps, such as measuring, pouring and packaging and use in the dye house. In addition to the dusting problems arising during the processing of these diazonium salts, the fine dust particles so created are a work hazard in the form of possible skin irritations and other health hazards among the workers.

It has now been found that improved stabilized diazonium compounds may be obtained by first reacting the diazotization product with a surface active agent, thereby effecting a partial stabilization of the diazonium compound with the surface active agent, and then effecting the remainder of the stabilization with one of the usual Fast Color Salt stabilizers mentioned above. The surface active agents which have been found effective are those of the anionic reactive group wherein the surface active agent contains an aliphatic hydrophobic group and an aliphatically linked hydrophilic group. Included in this group are surface active alkyl carboxylates, sulfonates, alcohol sulfates and phosphates. More specifically, there are included the following classes of surface active agents:

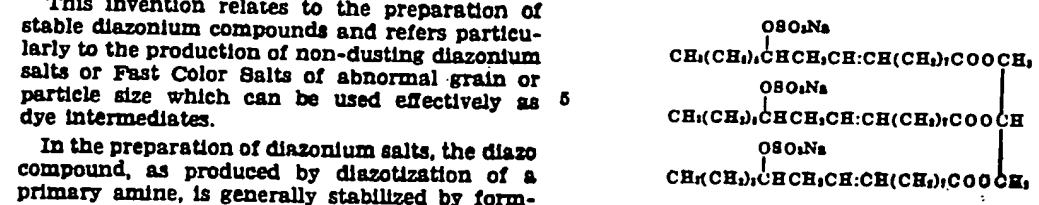
1. Alkali metal soaps such as sodium oleate,

$$CH_3(CH_2)_7CH{:}CH(CH_2)_7COONa$$

and sodium stearate

$$CH_3(CH_2)_{16}COONa$$

2. Sulfates of higher fatty acids such as sulfonated castor oil (triglyceride of ricinoleic acid)



3. Sulfonated higher fatty alcohols such as the cetyl sulfonic acid and the sodium salt of dodecyl sulfonic acid of USP 1,966,187.

4. Sulfated higher fatty alcohols such as sodium lauryl sulfate

$$C_{12}H_{25}OSO_3Na$$

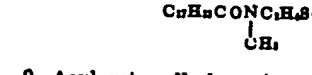
5. Phosphated higher alcohols such as the product known as W.A.35A.

$$(C_8H_{17})_6Na_4P_6O_{20}$$

6. Petroleum sulfonates such as the product known as Twitchell Oil 3X (Textile Chemical Specialty Guide, p. 74, 1946–7 Ed., Textile Book Publishers Inc., New York).

7. Sulfosuccinic acid esters such as a dibutyl ester of sodium sulfosuccinate and the diamyl ester of sodium sulfosuccinate.

8. Acylamidoalkylsulfonates such as the product known as Igepon T



9. Acylaminoalkyl carboxylates such as the sodium salt of oleyl sarcosine

10. Alkylsulfonamidoalkyl sulfonates such as the product known as Emulphor STU

$$CH_3(CH_2)_{13-15}SO_2NHCH_2CH_2SO_3Na$$

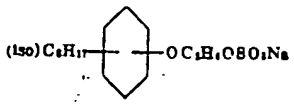
11. Alkylsulfonamido acetates such as the product known as Emulphor STH

$$CH_3(CH_2)_{13-15}SO_2NHCH_2COONa$$

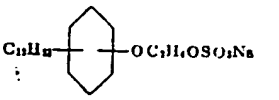
12. Mixed fatty acid monoglyceride sulfates such as the product known as Arctic Syntex M (Young and Coons' Surface Active Agents, page 119, Chemical Publ. Co., Brooklyn, N. Y., 1945).

3

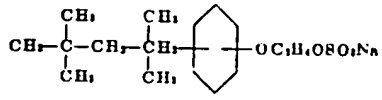
13. Alkylphenoxyalkyl sulfates such as the sodium sulfuric ester of isooctyl phenyl monoglycolether



The sodium sulfuric ester of dodecyl phenyl monoglycolether



and the sodium sulfuric acid ester of tetramethylbutylphenoxy ethanol



14. Amino soaps of fatty acids such as the stearic acid soap of 2-amino-1-butanol

The diazonium compounds stabilized by the surface active agents and the salts or acids generally employed as stabilizing agents in Fast Color Salts such as metallic chlorides, particularly the mercury, iron, zinc, cadmium, tin, antimony, platinum, gold, copper and arsenic chlorides, naphthalene sulfonic acids such as naphthalene-1.5-disulfonic acid, and fluoroboric acid are prepared by introducing a solution of the surface active agent into the diazotization solution. The combined diazo solution and surface active agent solution is then mixed with a solution containing the additional stabilizing agent. The exact order of mixing the reactants is not material, although it is preferable to initially mix the diazonium compound and the surface active agent. Thus the diazo and surface active agent can be combined first and the combined solutions added to a solution of the Fast Color Salt stabilizer (such as $ZnCl_2$); the Fast Color Salt stabilizer can be added to the mixture of the diazo plus the surface active agent; the diazo and the surface active agent may be run into the solution of the Fast Color Salt stabilizer simultaneously; or the latter may be added to the diazo solution prior to the surface active agent provided that the diazo solution is kept sufficiently dilute to prevent precipitation of the stabilized diazo before the surface active agent can act on it. When partial stabilization is effected with the surface active agents and stabilization completed with metallic chlorides or other known stabilizers, the stabilized diazonium salts precipitate out with a crystal structure which is distinguished from that of the crystal structures of diazonium salts produced from the same diazonium compounds but stabilized only with the usual or conventional stabilizers. This new crystal growth results in most cases either in the formation of larger crystals which may be different in structure from the crystal structure of the corresponding conventionally stabilized diazonium salts or in a change of degree of crystal aggregation, usually forming a greater degree of aggregation. In either case the product can be handled with greater ease and the solutions more efficiently filtered. It is also characteristic of the diazonium compounds stabilized in accordance with this invention the [redacted] greater degree of initial dryness is present in the filter cake.

4

The stabilization of the diazonium salts by means of the surface active agents of this invention thus results in an appreciable reduction of the water content of the filtered diazo cake, as a direct result of the change in crystal pattern or formation of larger crystals or crystal aggregates. As compared with ordinary Fast Color Salts which are stabilized only with the usual metallic salts, less water is held by the stabilized diazonium salts of this invention than is held by the Fast Color Salts, the comparative ratio being in the range of 25 to 50% for the conventionally stabilized diazonium salts to 5 to 15% for the diazonium salts stabilized in accordance with this invention. In order to obtain these results appreciable amounts of the surface active agent are used. Preferably about 5 to 20% of the surface active agent based on the amount of the diazo compound is employed. After filtering and dry mixing of the filter cake it may be noted that the dusting characteristic of the dry powdered product is decreased to a considerable degree and in many cases the resulting Fast Color Salts are rendered completely non-dusting. The resistance of the resulting stabilized diazonium salts or Fast Color Salts to decomposition during storage is also greatly improved by the use of the surface active agents. In order to inhibit decomposition of stabilized diazonium salts during storage, it is necessary that they be kept as dry as possible. This is accomplished generally by admixing with the stabilized diazonium salts anhydrous agents, such as the anhydrous sodium sulfate, anhydrous magnesium sulfate and partially dehydrated aluminum sulfate mentioned above. These compounds combine with water to form water of crystallization and thus keep the diazonium salts dry. The less water initially present in the filter cake the smaller the amount of dehydrating agent which must be used. In view of the large crystal structure or increased crystal aggregate formation resulting from the partial surface active compound stabilization of this invention, the filter cake contains only a fraction of the water which is present in the same diazonium salt stabilized by the usual complex salt formation with such compounds as $ZnCl_2$ and hence requires smaller amounts of the dehydrating agents. Also, the necessity for rigorous oven drying is eliminated in those cases where the Fast Color Salts stabilized with the usual stabilizers retain a large amount of water. In such cases it is normally necessary not only to hydraulically press them, but also to pre-dry them in ovens heated to approximately 40° C. for from 12 hours to 2 days in order to bring down the water content. Only after such rigorous drying treatment can they be dry mixed in the usual way. In the case of the surface active agent stabilized diazonium compound of this invention the stabilized diazonium salt will be in such a form that only a fraction of the water is retained. Hence dry mixing can be effected immediately with the dehydrating agents and the danger of at least partial decomposition of the diazo compound due to exposure to excessive heat for long periods of time is averted.

The following examples will serve to more fully illustrate this invention. It is understood, however, that the invention is not limited to the specific conditions obtaining in these examples which are intended to be illustrative of the best

manner to effect the products. Unless otherwise stated, the parts are by weight.

Example 1

The following mixture is slurried for 2 to 3 hours:

76 cc. water
50.6 cc. hydrochloric acid (21° Bé.)
33.6 gr. 4-nitro-o-anisidine

This mixture is then cooled to —10° C. and 13.8 gr. of 100% sodium nitrite are added as a 33% solution, care being taken that the temperature does not rise above +10° C. An excess nitrite test is maintained for ½ hour. Charcoal is added and the diazo solution filtered. A solution containing 6.0 gr. sodium oleate per 20 cc. of water is run into the diazo solution. The resulting solution is run into a solution containing 57.6 gr. 1.5-naphthalene disulfonic acid in 100 cc. of water. The precipitate is filtered, sucked dry, and dry mixed and standardized with sodium sulfate, aluminum sulfate and calcined magnesium sulfate.

The product obtained from this example has a coarser crystalline structure than the product obtained in a similar manner but without the addition of the sodium oleate. Because of this coarser crystalline structure the filter cake has a higher degree of initial dryness, thus requiring the addition of smaller amounts of the drying compounds used in dry mixing and lessening the tendency to dust of the dry particles.

Example 2

The following mixture is slurried for 2 to 3 hours:

76 cc. water
50.6 cc. hydrochloric acid (21° Bé.)
33.6 gr. 4-nitro-o-anisidine

The mixture is cooled to —10° C. and 13.8 gr. of 100% sodium nitrite are added as a 33% solution, care being taken that the temperature does not rise above +10° C. and excess nitrite test is maintained for half an hour. Charcoal is added and the diazo solution filtered. 16 gr. sulfonated castor oil are added to the diazo solution and a solution of 7 gr. of $ZnCl_2$ in a small amount of water is then added. The stabilized diazo is salted out with NaCl equivalent to 10% of the volume, filtered, dried, dry mixed and standardized with sodium sulfate, aluminum sulfate and calcined magnesium sulfate.

The product thus obtained has a coarser crystalline structure than the product obtained in a similar manner, but without the addition of the sulfonated castor oil. Because of this coarser crystalline structure the filter cake has a higher degree of initial dryness, thus requiring the addition of smaller amounts of the drying compounds used in dry mixing and lessening the tendency to dust of the dry particles.

Example 3

32.4 gr. 2.5-dichloroaniline are slurried with 46 cc. of water and then heated to 60° C. While applying fast agitation 78 cc. hydrochloric acid (21° Bé.) are added over a ten minute period. The mixture is cooled to zero degrees and 30 gr. of ice are added. 13.8 gr. of sodium nitrite are added as a 33% solution. The solution is then purified by treating with charcoal followed by filtering. 5.5 gr. of the sodium salt of dodecyl sulfonic acid are then added, followed by 7 gr. $ZnCl_2$ dissolved in a small amount of water. The

resulting stabilized diazo is salted out with NaCl equivalent to 10% of the volume, filtered, sucked dry, dry mixed and standardized with sodium sulfate, aluminum sulfate, and calcined magnesium sulfate.

The product obtained in accordance with this example has properties similar to the compositions of Examples 1 and 2 as compared with the product obtained in a similar manner to that of this example by omitting the sodium salt of dodecyl sulfonic acid.

Example 4

2.5-dichloroaniline is diazotized in the same manner as in Example 3. After purification of the diazo solution with charcoal and filtering, 9 gr. of sodium lauryl sulfate are added as an aqueous solution, followed by the addition of 7 gr. $ZnCl_2$ in a small amount of water. The resulting stabilized diazonium salt is salted out with NaCl equivalent to 10% of the volume, filtered, sucked dry, dry mixed and standardized with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The thus obtained product has properties similar to those of the product obtained in accordance with Example 3.

Example 5

33.6 gr. 5-nitro-o-anisidine are slurried with 100 cc. of water. To this are added 65 cc. hydrochloric acid (21° Bé.). The mixture is cooled to —10° C. and diazotized with 13.8 gr. $NaNO_2$ as a 33% solution. The solution is agitated for half an hour, treated with charcoal and filtered. There are then added 30 gr. of a phosphated higher fatty alcohol known as W.A.35A, said to have the formula $(C_8H_{17})_6NaP_3O_{20}$, which is dissolved in a small amount of water, and 7 gr. $ZnCl_2$ also dissolved in a small amount of water. The thus stabilized diazo compound is salted out with NaCl equivalent to 10% of the volume, filtered, sucked dry, dry mixed and standardized with sodium sulfate, aluminum sulfate, and calcined magnesium sulfate.

The product of this example has a coarser crystalline structure than the product obtained in a similar manner but without the addition of the phosphated higher fatty alcohol. Because of this coarser crystalline structure the filter cake has a higher degree of initial dryness, thus requiring a smaller amount of the drying compound used in dry mixing and lessening the tendency to dust of the dry particles.

Example 6

5-nitro-o-anisidine is diazotized in the same manner as in Example 5. After filtering the charcoal treated diazo solution, petroleum oil sulfonate such as Twitchell Oil 3X is added in the amount of 10% of the calculated amount of diazo compound or about 8 gr. dissolved in a small amount of water. An additional 7 gr. of concentrated aqueous solution of $ZnCl_2$ is added. The precipitate is filtered, sucked dry, standardized and dry mixed with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The product thus obtained has a coarser crystalline structure than the product obtained in a similar manner without the addition of the petroleum oil sulfonate. Because of this coarser crystalline structure, the filter cake has a higher degree of initial dryness, thus requiring the addition of smaller amounts of the drying compounds used in dry mixing and lessening the tendency to dust of the dry particles.

7

Example 7

28.3 gr. of 4-chloro-o-toluidine are added with agitation to a solution of 59 cc. (21° Bé.) hydrochloric acid in 80 cc. of water. The mixture is cooled to −5° C. and 13.8 gr. sodium nitrite in a 33% solution are added while maintaining the temperature below +10° C. The resulting diazo solution is purified by charcoal treatment and filtered. The diazo compound is then stabilized by adding a solution containing 7.5 gr. of the diamyl ester of sodium sulfosuccinate in 20 cc. of water, followed by the addition of 7 gr. $ZnCl_2$ dissolved in a small amount of water. The stabilized diazo is then salted out with sodium chloride equivalent to 10% of the volume, then filtered, sucked dry, standardized and dry mixed with sodium sulfate, aluminum sulfate, and calcined magnesium sulfate.

The product obtained in accordance with this example has a coarser crystalline structure than the product obtained in a similar manner omitting the addition of diamyl ester sulfosuccinate. Because of this crystalline structure the filter cake has a higher degree of initial dryness, thus requiring a smaller amount of the drying compounds used in dry mixing and lessening the tendency to dust of the particles.

Example 8

31.5 gr. of 5-chloro-o-anisidine are added to 115 cc. of water and the mixture heated together to 85° C. 27 cc. of hydrochloric acid (21° Bé.) are then added. The resulting solution is cooled to −5° C. and an additional 27 cc. of 21° Bé. hydrochloric acid are added. The solution is again cooled to −5° C. and 13.8 gr. sodium nitrite are added as a 33% solution. The resulting solution is purified by the addition of charcoal and filtered. To the filtered solution there is added a solution of 5 gr. of an acylamidoalkylsulfonate having the formula

$$C_{17}H_{33}CON(CH_3)C_2H_4SO_3Na$$

in 20 cc. of water. A concentrated aqueous solution of 7 gr. of $ZnCl_2$ is then added. The resulting stabilized diazo compound is then salted out very slowly with NaCl equivalent to 10% by volume. The precipitate is filtered, sucked dry, standardized and dry mixed with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. A product is obtained which has a coarser crystalline structure than that obtained in a similar manner without the addition of the acylamidoalkylsulfonate. This coarser crystalline product has a higher degree of initial dryness, thus eliminating the necessity for special drying procedures and requiring the addition of smaller amounts of the drying compounds used in dry mixing. The tendency to dust of the dry powder is also considerably reduced.

Example 9

28.3 gr. of 4-chloro-o-toluidine are added to 115 cc. of water and the solution heated to 85° C. 27 cc. of 21° Bé. HCl are then added and the solution cooled to −5° C. while adding an additional 27 cc. of 21° Bé. HCl. The solution is again cooled to −5° C. after which 13.8 gr. of sodium nitrite are added as a 33% solution. The resulting diazo compound is purified by the addition of charcoal and filtered. To the filtered diazo solution there are added 4 gr. of the sodium salt of oleyl sarcosine in 20 cc. of water. A concentrated aqueous solution of 7 gr. of $ZnCl_2$ are

8

then added and the stabilized diazo compound resulting from these additions is salted out by adding slowly NaCl equivalent to 10% by volume. The precipitate is filtered, sucked dry, standardized and dry mixed with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The product thus obtained has characteristics similar to the product of Example 8.

Example 10

31.5 gr. of 4-chloro-o-anisidine are added to 115 cc. of water and the solution heated at 85° C. 27 cc. of 21° Bé. HCl are then added. The resulting solution is cooled to −5° C. and an additional 27 cc. of 21° Bé. HCl are added. The solution is again cooled to −5° C., after which 13.8 gr. sodium nitrite are added as a 33% solution. The resulting diazo solution is purified by the addition of charcoal and filtered. To the filtered solution there are then added 5 gr. of a sodium salt of an alkyl sulfonamido alkyl sulfonate having the general formula

$$CH_3(CH_2)_{13-16}SO_2NHCH_2CH_2SO_3Na$$

in a solution of 20 cc. of water. A concentrated aqueous solution containing 7 gr. $ZnCl_2$ is then added. The resulting stabilized diazonium salt is salted out by slowly adding an amount of NaCl equivalent to 10% of the volume. The precipitate is filtered, sucked dry, standardized and dry mixed with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The product obtained has a coarser crystalline structure than that obtained in a similar manner without the addition of the sodium alkyl sulfonamido alkyl sulfonate. This coarser crystalline product in the form of the filter cake has a higher degree of essential dryness, thus eliminating the necessity for special drying procedures and reducing the amount of drying compounds required in the dry mixing. The tendency to dust of the dry particles is also reduced.

Example 11

33.6 gr. 5-nitro-o-anisidine are slurried with 100 cc. of water. To this slurry are added 65 cc. of 21° Bé. HCl. The mixture is cooled to −10° C. and there are then added 13.8 gr. sodium nitrite as a 33% solution. The resulting diazotized solution is agitated for half an hour, clarified by the addition of charcoal and filtered. To the filtered diazo solution there are added 5 gr. of the sodium alkyl sulfonamido acetate having the formula

$$CH_3(CH_2)_{13-16}NHCH_2COONa$$

dissolved in 15 cc. of water. A concentrated aqueous solution of $ZnCl_2$ is then added. The stabilized diazonium salt thus obtained is salted out by the addition of an amount of NaCl equivalent to 10% of the volume. The precipitate is filtered, sucked dry, standardized, and dry mixed with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The crystalline product thus obtained has characteristics similar to those obtained as the product of Example 10.

Example 12

33.6 gr. 2-nitro-p-anisidine are slurried in 46 cc. of water. 53 cc. of 21° Bé. HCl are added to the slurry and the resulting solution is cooled to 5° C., after which 13.8 gr. sodium nitrite are added as a 33% solution. This diazotization solution is then salted to saturation, clarified by treatment with charcoal and filtered. To the filtered solution there are added 9 gr. of sulfate of

mixed fatty acid monoglycerides known as Arctic Syntex M (Young and Coon's Surface Active Agents, p. 119) dissolved in 30 cc. of water. To this solution there are added 7 gr. of $ZnCl_2$ in concentrated aqueous solution. The thus stabilized diazonium salt is then salted out, filtered, sucked dry, standardized and dry mixed with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The product thus obtained has a coarser crystalline structure than that obtained in a similar manner but without the addition of the sulfated mixed fatty acid monoglyceride.

Example 13

33.8 gr. 2-nitro-p-anisidine are diazotized in the same manner as in the preceding example. To the filtered diazo solution there are added 7 gr. of the sodium sulfate ester of isooctyl phenyl monoglycolether dissolved in 20 cc. of water. A concentrated aqueous solution of 9.5 gr. of cadmium chloride is then added. The resulting product is salted out and finished in the same manner as the product of the preceding example. It has similar characteristics to the product of that example.

Example 14

2-nitro-p-anisidine is diazotized in the same manner as in Example 12. To the filtered diazo solution there are added 4.5 gr. of the stearic acid soap of 2-aminobutanol followed by the addition of 7 gr. $ZnCl_2$ in a concentrated aqueous solution. The resulting product is salted out and finished in the same manner as in the case of Example 12. Its properties are similar to those of the product of Example 12.

Example 15

The following mixture is slurried for 1 hr.:

24.4 gr. dianisidine
532 cc. water
63 cc. 21° Bé. HCl

The mixture is cooled to 5° C. and tetrazotized in 3–4 hr. with 13.8 gr. sodium nitrite as a 33% solution. The temperature should be held below 10° C. An excess nitrite test is maintained for 30 min. The diazonium solution is clarified by charcoal-treatment followed by filtration. 9 gr. of sodium lauryl sulfate are added and a concentrated aqueous solution of 7 gr. of $ZnCl_2$. The stabilized diazo is salted out with an amount of NaCl equivalent to 10% of the volume, filtered, sucked dry, and dry mixed and standardized by the addition of sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The crystalline product thus obtained is similar in characteristics to the product of Example 10.

Example 16

The following mixture is slurried for 1 hr.:

42.8 gr. 4'-methoxy-4-aminodiphenylamine
555 cc. water
107.5 cc. 21° Bé. HCl

The mixture is cooled to 0° C. and 13.8 gr. sodium nitrite are added as a 15% solution. The temperature is held below 10° C. for several hours. An excess nitrite test is maintained for 30 minutes. The diazonium crystallizes out. This slurry is heated for 1 hr. at 50° C. to complete solution, then purified by charcoal treatment and filtered. 7.5 gr. diamyl ester of sodium sulfosuccinate in 20 cc. water are added while still warm. The stabilized diazonium salt thus obtained is salted out by the addition of an amount of NaCl equivalent to 15% of the volume while cooling to about 10° C. The precipitate is filtered, sucked dry, and standardized and dry mixed with sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The crystalline product thus obtained has characteristics similar to those obtained as the product of Example 10.

Example 17

The following mixture is slurried for 1 hr.:

51.2 gr. 4'-amino-6'-methyl-m-benzanisidide
63 cc. 21° Bé. HCl
160 cc. water

The mixture is cooled to 5° C. and diazotized in 3–4 hr. with 13.8 gr. sodium nitrite as a 33% solution. The temperature should be held below 15° C. An excess nitrite test is maintained for 30 minutes. The diazonium solution is clarified by charcoal treatment followed by filtration. 16 gr. sulfonated castor oil are added to the diazo solution and a solution of 7 gr. $ZnCl_2$ in a small amount of water. The stabilized diazo is salted out with NaCl equivalent to 10% of the volume, filtered, sucked dry and dry mixed and standardized by the addition of sodium sulfate, aluminum sulfate and calcined magnesium sulfate. The product has characteristics similar to the product of Example 10.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stable diazonium salt comprising a diazotized aromatic compound combined with an anionic surface active agent containing an aliphatic hydrophobic group and an aliphatically linked hydrophilic group and another compound capable of forming a salt with the diazonium compound.

2. A stable diazonium salt comprising a diazotized aromatic compound combined with an anionic surface active agent containing an aliphatic hydrophobic group and an aliphatically linked hydrophilic group and another compound capable of forming a complex salt with the diazonium compound, the surface active agent being present in an amount equal to from 5 to 20% of the amount of the diazonium compound.

3. A stable diazonium salt comprising a diazotized aromatic compound combined with a mixture of an anionic surface active agent containing an aliphatic hydrophobic group and an aliphatically linked hydrophilic group and zinc chloride.

4. A stable diazonium salt comprising a diazotized aromatic compound combined with a mixture of an anionic surface active agent containing an aliphatic hydrophobic group and an aliphatically linked hydrophilic group and cadmium chloride.

5. A stable diazonium salt comprising a diazotized aromatic compound combined with a mixture of an anionic surface active agent containing an aliphatic hydrophobic group and an aliphatically linked hydrophilic group and 1.5 naphthalene disulfonic acid.

6. A stable diazonium salt comprising a diazotized aromatic compound combined with a mixture of sulfonated castor oil and zinc chloride.

11

7. A stable diazonium salt comprising a diazotized aromatic compound combined with a mixture of sodium oleate and 1.5 naphthalene disulfonic acid.

8. A stable diazonium salt comprising a diazotized aromatic compound combined with a mixture of the sodium sulfate ester of isooctylphenyl

12

glycol ether and cadmium chloride.

W. D. HERRIDGE,
140 Wellington St.,
Ottawa, Ont.,
Patent Agent
of the Applicants.

EDMOND CLOUTIER, C.M.G., O.A., D.S.P., Queen's Printer and Controller of Stationery, Ottawa, 1955